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Composition and Conductivity-type Analysis of Spray Pyrolysed ZnS Thin Films using Photoluminescence

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Abstract

Photoluminescence (PL) technique has been employed to successfully determine the composition and conductivity type of spray pyrolysed ZnS thin films. Aiming to improve the optoelectronic properties, ZnS thin films were deposited using different precursors for zinc. Variation in Zn:S ratios were also tried along with a variation in precursor which naturally brings compositional variations which in turn reflects in the PL spectrum. From the XRD patterns a modification in crystal structure was observed in the case of acetate based ZnS films. This modification reflected as a shift in the PL peak position. Acetate based films exhibited conductivity type variation: films with low sulphur content were n-type and those which were rich in sulphur were p-type.

Keywords: Photoluminescence; ZnS thin films; chemical spray pyrolysis; wurtzite; sphalerite; conductivity

1. Introduction

The wide band gap and the presence of large number of point defects present within the band gap make ZnS a most wanted member of the optoelectronics industry [1]. Studies on ZnS in thin film as well as nano particle form have been an active research topic for the past few decades [2, 3]. It can be used for various device applications as blue light emitting diodes, electro optic modulators, n-type window material in solar cells etc owing to its strong photo-, electro- and cathodoluminescent properties [4]. Thus photoluminescence (PL) is one among the strong analytical tools which yields information on the point defects and surface states present in the material [5]. The slight problem concerning ZnS is that there is

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not much consensus on the defects responsible for broad sub band gap luminescence. Different explanations have been given for the same luminescence band depending on the mode and conditions of preparation. The luminescence properties of un-doped ZnS are decided by the composition and on the concentration of luminescent centres available [6]. Thus in order to get a fair assessment of what might be the cause of luminescence, the best way is to play with the stoichiometry. Though numerous techniques have been reported for deposition of ZnS thin films [7], we have adopted the cost effective and scalable chemical spray pyrolysis (CSP) technique [8] for deposition. In the present work we have presented some interesting observations on how PL technique can be used for analysing the composition as well as to understand the conductivity type of ZnS samples. It has earlier been observed that a variation in precursor could bring profound changes to the optoelectronic properties of thin films deposited [9]. So ZnS thin films deposited using two different precursors for zinc, i.e., zinc acetate and zinc chloride, deposited for various Zn:S ratios were chosen for study.

2. Experimental details

ZnS thin films were deposited using two different precursors for zinc-zinc acetate and zinc chloride, and thiourea was chosen as the precursor for sulphur. The respective precursor solutions were mixed together and stirred well for homogeneity. 50 ml of precursor solution was sprayed at a spray rate of 5 ml/min onto soda lime glass substrates maintained 450ºC. Chloride based films were named A and acetate based films were named B respectively. Films of batch A and B were prepared by varying the Zn:S ratio as 1: 0.5, 1, 2, 3, 4 and 5 respectively. Room temperature PL measurements were done on all the samples prepared. The samples were excited using the 325 nm line of He-Cd laser (Kimmon Koha Pvt. Ltd; output power 20 mW). The emission was collected using CCD coupled spectrophotometer (Ocean Optics USB 2000) and interfaced to the computer using custom made software OOIbase32.

3. Results and discussion

The PL signal obtained is quite sensitive to the impurities or defects present within the sample. In the case of ZnS, the possible defects are vacancies of zinc (V_{Zn}), vacancies of sulphur (V_S) (which are acceptor and donor levels respectively) whereas interstitials of zinc (Zn_I) and sulphur (S_I) form donor and acceptor levels respectively. The room temperature PL spectra of batch “A” samples prepared for various Zn:S ratios are shown in Fig. 1 below.

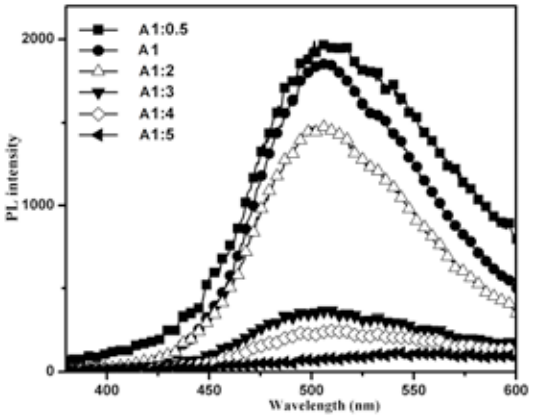

Fig. 1. Room temperature PL spectra of batch “A” films prepared for various Zn:S ratios.

It can be seen that the emission is quite asymmetric and broad, peaking in the green (~510 nm) and tail extending up to the red. Broad emission in the green region has been observed by various groups [10] and many reasons have been attributed for the same. The transition may be a free to bound one or from any donor to acceptor. ZnO is an inevitable phase that forms along with ZnS [11] and it is quite unavoidable in CSP as it is a non vacuum process. Green luminescence is a prominent characteristic of ZnO also. Emission around 470 nm and 550 nm has also been reported for ZnS thin films [12, 13].

It can be seen that as the concentration of sulphur increases the intensity of the emission decreases. The emission might be arising from a donor created by vacancy of sulphur which gets reduced with an increase in concentration of sulphur. The capture cross section of this level might be quite large as compared to other levels which explain the prominence of this emission. Structural studies done using Rigaku X Ray diffractometer indicate that the peaks obtained at $2\theta = 27.35, 28.77, 48.17^{o}$ in the XRD pattern match well with the JCPDS card no. 80-0007 indicating the presence of hexagonal wurtzite structure (Fig. 2).

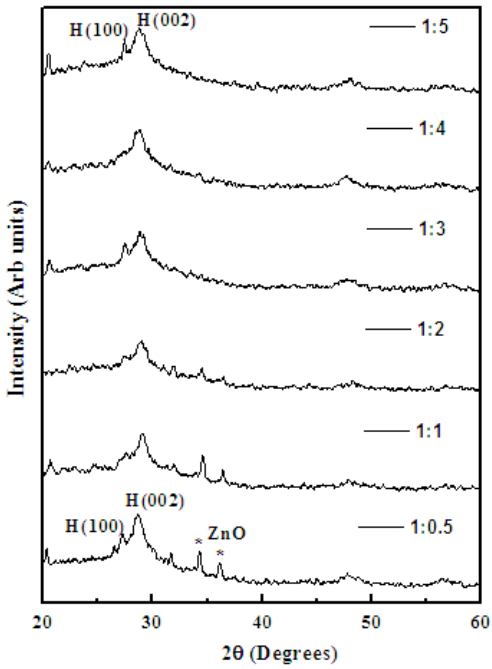

Fig.2. XRD pattern of batch “A” samples prepared for various Zn:S ratios.

It is quite well known that wurtzite phase formation is more favoured by predominantly ionic systems [13] and the incorporation of Cl^{-} ions in sulphur sub lattice favours this situation. Hot probe conductivity measurements indicate that all films of batch “A” are n-type. Room temperature PL spectra of batch “B” samples are given in Fig. 3.

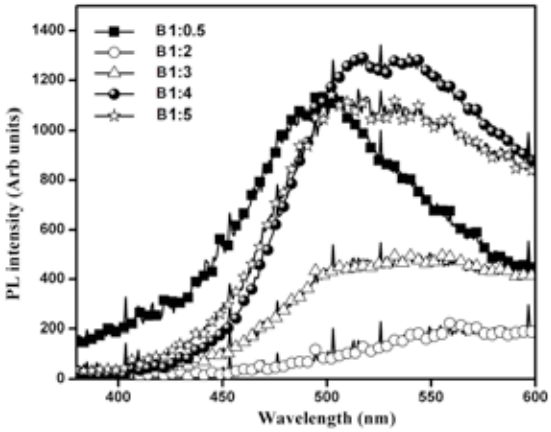

Fig. 3. Room temperature PL spectra of batch "B" films prepared for various Zn:S ratios.

As for batch "A" samples, the emission here is broad and asymmetric. A significant shift can be observed for PL peak position with increase in sulphur concentration. For sample B1:0.5 where the sulphur concentration is quite low, the PL peak position is centred at around 500 nm. A small peak at around 440 nm can be resolved for this sample, which has been reported to arise at the predominance of wurtzite phase of ZnS. For samples with higher sulphur content, the PL peaks have been red shifted. Structural studies indicate that for samples with low sulphur content, the orientation of the films were in the (002) plane characteristic of wurtzite ZnS. Peaks corresponding to ZnO were also observed in the XRD patterns for low sulphur concentration samples. With increase in sulphur content, XRD peaks at $2\theta = 28.62, 47.46^{o}$ were found to appear which correspond to the (111) and (220) phases of sphalerite ZnS [JCPDS card no. 05-0566] (Fig. 4).

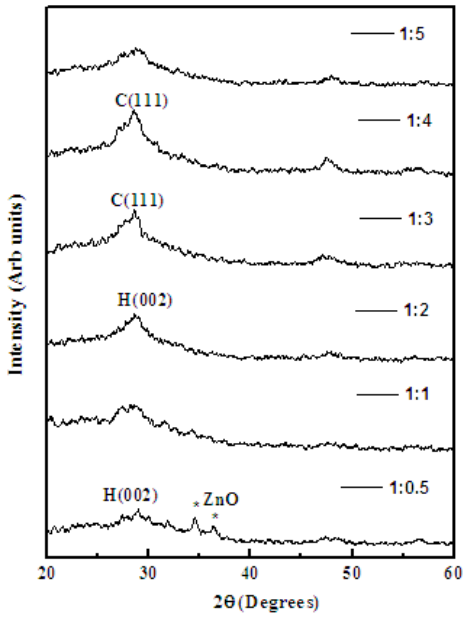

Fig. 4. XRD pattern of batch "B" samples prepared for different Zn:S ratios.

Thus there is a modification in crystallite structure with increase in sulphur concentration. It has already been reported that crystal structure modification from wurtzite to sphalerite can be observed as a red shift in PL peak position [13] which we have also observed with the emission that we have obtained. Hot probe conductivity measurements indicate that for low sulphur concentrations the films were n-type and for higher sulphur concentrations the films were p-type.

Thus so far from our observations we can see that chloride based films (batch "A") are n-type for all Zn:S ratios whereas acetate based films (batch "B") are n-type when Zn:S ratio is high (when sulphur content is low) and p-type when Zn:S ratio is low (for high sulphur content). From our observations we presume that Cl^- ions have a role to play in deciding the type as well as structure. For that, we decided to purposefully incorporate chlorine into acetate based films. Chlorine doped acetate based films were prepared and this batch of films were named "C" respectively. Room temperature PL studies of batch "C" samples were done. It could be observed that there was no shift in the PL peak position (Fig. 5).

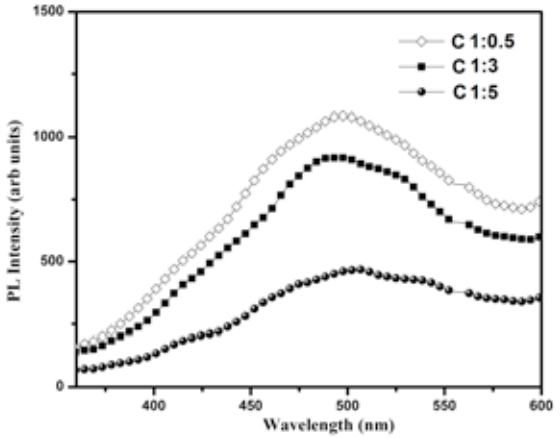

Fig. 5. PL spectrum of batch "C" samples for various Zn:S ratios.

Moreover it can be observed that peaks from 400 to 600 nm etc are present which have already been reported for ZnS. Hot probe measurements indicate that there is no type conversion for this set of samples. The XRD pattern of batch "C" films is shown in Fig. 6. The XRD peaks at $2\theta = 27.35, 28.77, 48.17^o$ in the XRD pattern match well with the JCPDS card no.80-0007 indicate a predominant wurtzite structure for all Zn:S ratios. No crystal structure variation is observed in batch "C" samples.

Thus it can be seen that incorporation of Cl^- ions in sulphur sub lattice is responsible for this behaviour. Thus it may be thought of that chlorine might be forming a strong donor level which makes the film n-type. This might well be the reason as to why chloride based films were n type for all Zn:S ratios.

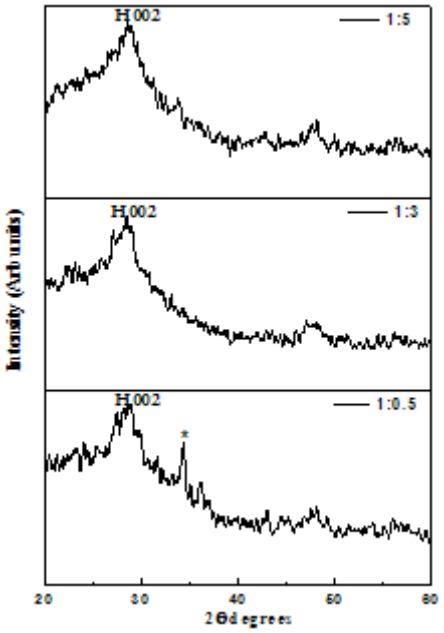

Fig. 6. XRD pattern of batch "C" samples prepared for different Zn:S ratios.

4. Conclusion

ZnS thin films deposited using different zinc precursors for various Zn:S ratios were analysed using PL. It could be observed that variation in Zn:S ratio affects the PL intensity in the case of both chloride based as well as acetate based ZnS samples. With increase in sulphur concentration the intensity of the broad green emission decreases without any change in peak position for chloride based samples. For acetate based samples on the other hand with increase in sulphur concentration there is a modification in the crystal structure from wurtzite to sphalerite and the conductivity type of films changes from n to p. This has been manifested in the PL spectrum as a red shift of the observed green emission. The reason why chloride based films exhibit no type conversion might be because of a strong donor created by incorporation of chlorine which ensures that the samples are n-type. Chlorine doped acetate based films exhibited no type conversion (were n type for all Zn:S ratios) and there was no peak shift observed in the PL spectrum, which confirms the role of a donor level due to chlorine in deciding the structure and conductivity type.

Acknowledgements

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